

Reactions of Stoichiometric Intumescent Paints

Heinrich Horacek

A-4048 Puchenau, Am Wiesenrain 1, Austria

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ABSTRACT: Under the influence of heat intumescent paints with stoichiometric compositions decomposed to defined compounds: Ammonium polyphosphate degraded to polyphosphoric acid and ammonia. Polyphosphoric acid reacted with pentaerythritols and glycerol to cyclic phosphoric acid esters, which were identified as the blowing agents. Melamine and polyphosphoric acid combined to melamine polyphosphate and dipolyphosphate. In further degradation of polyphosphoric acid, it dehydrated to

phosphorus pentoxide, which reacted with titanium dioxide further to titanium pyrophosphate. Intumescent paints with higher efficiency could be developed by the addition of glycerol, which reacted to phosphoric esters with lower temperatures of decomposition. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1745–1756, 2009

Key words: coatings; degradation; differential scanning calorimetry; intumescence; thermogravimetric analysis

INTRODUCTION

Intumescent paints with a production volume of 15,000 tons a year are a small niche in the huge European market of varnishes. In general, paints comprising binders, pigments, solvents, and additives are not stoichiometric formulations. Intumescent paints are not only drying and curing but reactive. In the event of fire, the intumescent ingredients react to form blowing agents, which expand the protective films to insulating foams. The cellular films impede the contact with air, insulate against further increase in temperature, and delay decomposition and burning. New developments are focused on reduction of costs by improved efficiency. For the case of 2 mm dry film thickness 23 €/m² are the costs of the paint and 70 €/m² are the estimated costs for application. The certificates of paints in Europe guarantee burning classes F30, F60, or F90 for a declared dry film thickness on a steel column with a defined horizontal perimeter to area factor H_p/A . The figures of the burning classes indicate the time until the protected column reaches 500°C. At that temperature, steel loses 50% of its mechanical strength. Low costs are achievable by a small dry film thickness dft , a low dry density dd , a low price per kg, and a high solid content sc of the varnish. The cost of paints is given by eq. (1)

$$\text{Cost of paint (€/m}^2\text{)} = dft \text{ (mm)} \times dd \text{ (g/cm}^3\text{)} \\ \times (\text{€/kg}) \times 100/sc \text{ (\%)} \quad (1)$$

The costs of application (€/m²) are even more severe. They are fixed by the labor costs (€/h), the consumption of time (h/m²) for the application of one stage per m² and the numbers of coats (layers) necessary [eq. (2)].

$$\text{Costs of application (€/m}^2\text{)} = \text{labor costs (€/h)} \times \\ [(h/m^2) \times \text{number of layers}] \quad (2)$$

The number of layers are determined by the ratio of necessary dry film thickness and the maximum dry film thickness applicable by one procedure, for instance 0.250 mm as in eq. (3)

$$\text{Number of stages} = dft/0.250 \quad (3)$$

These equations show that the overall target is a low dft . Although there have been studies in the past concerning the mechanism of thermal degradation of fire retardant melamine salts¹ and of intumescent coatings,^{2–6} they did not answer the question what measures to take for increased efficiency. Stoichiometric intumescent paints require a deeper insight, and due to better understanding, possible improvements.

EXPERIMENTAL

Materials

In Table I, five different intumescent paints were formulated in such a way that stoichiometric

Dedicated to my friends, the chemists G. Bihlmayer and H. Czepel, on the occasion of their 70th birthday.

Correspondence to: H. Horacek (heinrich.horacek@aon.at).

TABLE I
Compositions of Dry Films for Intumescent Paints 1–5

Ingredients (MW)	No. 1		No. 2		No. 3		No. 4		No. 5	
	%	mols	%	mols	%	mols	%	mols	%	mols
APP (97)	41.0	12	26.4	2	36.5	6.5	37.1	12	21.0	2
PER (136)			18.5	1					14.6	1
DPER (254)	8.9	1			14.7	1	8.1	1		
GLY (92)									9.9	1
Mel (126)	8.9	2	17.1	1	11.0	1.5	8.0	2	13.6	1
TiO ₂ (80)	16.9	6	10.9	1	18.5	4	15.3	6	17.3	2
PVAc (86)	15.2	5	17.6	1.5					18.6	2
PVC (62.5)					16.3	4.5				
Epoxy (876)							27.9	1		
Additives	9.1		9.5		3.0		3.6		5.0	
Sum	100 (2838 g)		100 (735 g)		100 (1726 g)		100 (3139 g)		100 (926 g)	

compositions were achieved. For simplification, the influence of additives was ignored and only considered in the weight losses. Moreover, possible reaction products were synthesized as reference products. The ingredients used were provided from following companies:

- Ammonium polyphosphate APP Exolit 422 (Clariant)
- Pentaerythritol PER (Perstorp)
- Dipentaerythritol DPER (Perstorp)
- Glycerol GLY (Aldrich)
- Melamine Mel (BASF)
- Titanium dioxide TiO₂ Kronos 2300 (Kronos)
- Polyvinylacetate PVAc Mowilith DM 230 (Celanese) copolymer of vinyl acetate and vinyl ester of versatic acid
- Polyvinylchloride PVC Vinnol H15/50 (Wacker) copolymer of 85% vinyl chloride and 15% vinyl acetate
- Epoxy Beckopox EH 613, Beckopox EP 385 (Cytec) isophorone diamine C₁₁H₂₀N₂O and DGEBA C₂₁H₂₄O₄ Epoxy/amine = 1/0.5

As possible reaction products were considered:

- Bicyclopentaerythritol phosphate BCPP CAS 5301-78-0 NH 1197 (Great Lakes Chemical)
- Melamine phosphate MelP CAS 20208-95-1
- Melamine diphosphate MelP2 CAS 1554-60-3
- Dipentaerythritol phosphoric acid ester DPERP
- Dipentaerythritol diphosphoric acid ester DPERP2

Synthesis of melamine phosphate and diphosphate

Chemicals used: melamine (BASF), 75% phosphoric acid. A 2000-mL three-necked round-bottom flask was equipped with a mechanical stirrer, reflux condenser, thermometer, and addition funnel. Two hundred eighty-one grams melamine was added to

500 mL water. Under stirring, 291 g or 582 g 75% phosphoric acid were added within 30 min. Then the temperature was raised to 100°C and a vacuum of 18 Torr was applied. Melamine phosphate or melamine diphosphate were obtained as white residues: 499 g or 717 g (100% of the theoretical yield).

Synthesis of dipentaerythritol phosphoric acid esters

Chemicals used: dipentaerythritol (Perstorp), phosphorus oxychloride (Aldrich) dipentaerythritol phosphoric acid esters were synthesized by analogy to pentaerythritol phosphoric acid esters.⁷ A 2000-mL three-necked round-bottom flask was equipped with a mechanical stirrer, reflux condenser, thermometer, addition funnel, dry N₂ inert, and aqueous NaOH trap. The flask was charged with 1050 mL dioxane and 254 g (1 mole DPER). The mixture was stirred under flow of N₂ and heated. When the temperature reached 95°C 50% (76, 75 g, respectively, 159.5 g) of the total POCl₃ was added. The rest of the POCl₃ was charged at such a rate as to keep the rate of HCl evolution to no more than 2%/min. When 92% of the theoretical amount of HCl was evolved in about 7 h, the reaction mixture was slowly cooled to room temperature and filtered. The white solid was washed once with 200 mL of dioxane and twice with 500 mL *n*-hexane. The powdery products were

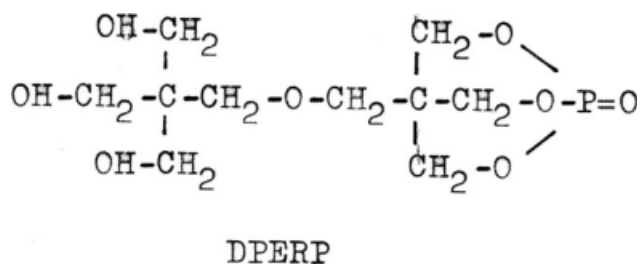


Figure 1 DPERP1 dipentaerythritol phosphate C₁₀H₁₉O₈P₁ MW = 298 g/mol.

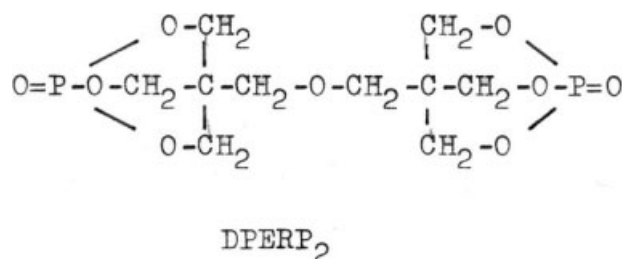
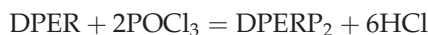


Figure 2 DPERP₂ dipentaerythritoldiphosphate C₁₀H₁₆O₉P₂ MW = 342 g/mol.

dried at 70°C under vacuum. The yield was 268 or 308 g (90% of the theoretical yield) Following reactions took place: DPER + POCl₃ = DPERP + 3HCl

$$\text{MW: } 254 + 153.5 = 298 + 109.5$$

DPERP in Figure 1 melted at 280°C and had a phosphorus content of 10.4% in theory and 10.3% found.



$$\text{MW: } 254 + 307 = 342 + 219$$

DPERP₂ in Figure 2 melted at 272°C and showed a phosphorus content of 18.1% in theory and 18.0% found.

APPARATUS

These compounds and the main ingredients of the paints were investigated by differential scanning calorimetry (DSC), by thermo mechanic analysis (TMA), and thermal gravimetric analysis (TGA) on a Mettler Toledo TMA/SDTA 840 with TGA/SDTA 851 Modul. In the case of TGA and DSC measurements, the samples were placed in aluminum oxide crucibles of 900 μL volume (ME 51119,960) with 12-mm diameter covered by punctured lids. The TGA measurements took place under air with 50 mL/min rate and those of DSC under nitrogen with 80 mL/min at heating rates between 5 and 50 K/min. The TMA investigations were performed in aluminum oxide crucibles with 7-mm diameter and 4.6-mm height covered by 6-mm diameter lids in air at a heating rate of 50 K/min. TGA diagrams provided the residues R (%) a dependent function of temperature. By differentiation, those temperatures (*T*) were obtained at which decomposition proceeded at highest speed. When the samples were heated at different heating rates *v* (K/min), the energies of activation *E* (kJ/g) could be calculated. The inverse peak reaction temperatures 1/*T* were plotted against the lg*v* and the inclination dl*g**v*/d(1/*T*) was deter-

mined.⁸ By eq. (4), the energies of activation were calculated

$$\begin{aligned} \text{dl}g\text{v}/\text{d}(1/T)[R/(0.4567 \times \text{MW})] \\ = \text{dl}g\text{v}/\text{d}(1/T)(18.2/\text{MW}) = -E(\text{kJ/g}) \quad (4) \end{aligned}$$

In eq. (4), *R* stands for the ideal gas constant and MW for molecular weight.

From DSC data, the heats of decomposition *h* (kJ/g) and the temperatures of decomposition *T* (°C) were obtained.

TMA measurements supplied the information on the expansion factor EF, which is defined as the observed volume (*V*) divided by the volume of the untreated sample (*V*₀) minus 1 in eq. (5)

$$\text{EF} = (V/V_0) - 1 \quad (5)$$

Further, the onset temperatures of expansion, the temperatures of maximum expansion, and the amounts of maximum expansion EF max were determined. Under the assumption of no losses and no viscoelastic contra-forces, EF max × *V*₀ was equivalent with the gasses produced. The moles of gasses evolved *n* could be calculated with the help of the ideal gas law

$$n = V_0 \times \text{EFmax} \times w / [22400 \times (1 + T(^{\circ}\text{C})/273)] \quad (6)$$

where *w* is the weight of the investigated sample and *T* is the temperature of expansion.

The heats of combustion (*h*) comb were investigated in a calorimeter according to DIN 51,900 Teil 2 (1977) Heizwertbestimmung.

The five varnishes were applied on closed columns with a horizontal perimeter to area ratio Hp/A = 270 m⁻¹ by brush. The dry film thickness was 1 mm in average. Fire tests were performed in a furnace heated according to the ISO curve. The temperatures of the samples were measured by fixed thermocouples.

RESULTS

TMA measurements

Besides pentaerythritol dipentaerythritol was applied. DPER showed a desired lower water solubility (Table II). Powder mixtures were prepared comprising APP, PER, Mel and APP, DPER, Mel and were

TABLE II
Water Solubility of Pentaerythritol PER and Dipentaerythritol DPER

Temperature (°C)	PER (g/100 g water)	DPER (g/100 g water)
25	7.2	0.3
50	16.1	1.1
90	51.9	6.1

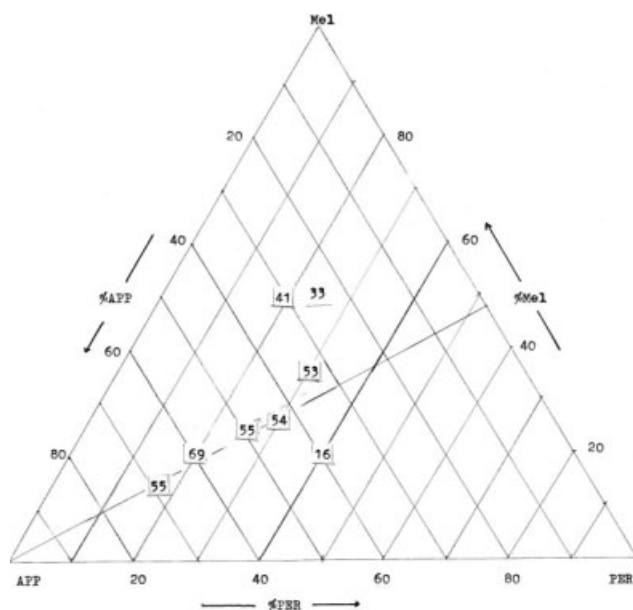


Figure 3 TMA of powder mixtures of APP, PER, and melamine: figures represent the maximum expansion factor EF max.

submitted to TMA measurements at a heating rate of 50°C/min, loaded by 0.02N under air. In Figures 3 and 4, the fields of mixtures of the three components and their maximum expansion factors at 390°C as numbers were depicted.

The compositions of APP, PER, Mel exerted the highest expansions along formulations with 1 mol PER and 1 mol Mel with APP contents of 1 mol or higher. The highest maximum expansion factor of 69 exerted the mixture with 4 moles APP.

Mixtures of APP, DPER, Mel exhibited the same behavior for the constant ratio of 1 mol DPER and 2 mol Mel with APP amounts of 2 moles or higher. The highest maximum expansion factor 65 exerted the mixture with 4 moles APP.

Without losses of gas and under neglecting the viscoelastic contra-forces the maximum expansion factor should correlate with the amount of gas evolved. When the ideal gas law eq. (6) was applied, the moles of gasses (n) could be determined and amounted 1.7 for the 4 M APP, 1 M Mel, 1 M PER mixture (650 g) and 2.2 for the 4 M APP, 2 M Mel, 1 M DPER mixture (894 g).

$$n = 2.1 \times 69 \times 650 / [22.400(1 + 390/273)] = 1.73 \quad (6a)$$

$$n = 2.1 \times 65 \times 894 / [22.400 \times 81 + 390/273] = 2.24 \quad (6b)$$

The specific volumes (V_o) of all mixtures were about 2.1 cm³/g. At 390°C, they expanded to 69 and 65 times of their original volumes.

In Figure 5, the dry films of the paints No. 1, No. 2, and No. 3 started expansion at 350°C and reached

a maximum expansion at 390°C. Paint No. 4 expanded to a low extent. Paint No. 5 started expansion at 300°C.

The maximum expansion factors of the dry films with 10–35 were lower than those of the powder mixtures with 65–69 and as a result of eq. (6) 0.3–0.8 moles of gasses were calculated in Table III using a specific volume of V_o of 0.65 mL/g. The reduced expansions in films indicated losses of gasses in combination with contra-forces.

A high expansion factor at a deep temperature of onset as well as a stable foam of low heat conductivity were thought to be responsible for the efficiency of an intumescent paint. Both powder mixtures and paints reached maximum expansion at 390°C only paint 5 with glycerol reached maximum expansion at 300°C. All binders reduced the maximum expansion to some extent but the cross-linked binder in paint 4 to the highest extent. The calculated moles of gasses evolved indicated BCPP and DPERP₂ as blowing agents.

TGA and DSC measurements

The components of the paints were subdued to differential scanning calorimetry (DSC) in nitrogen and to thermogravimetric analysis TGA in air or nitrogen at a heating rate of 20°C/min or at varying heating rates. The application of these methods provided as results the temperatures of degradation T , the residues R , the heats of decomposition h , and the energies of activation EA in Table IV.

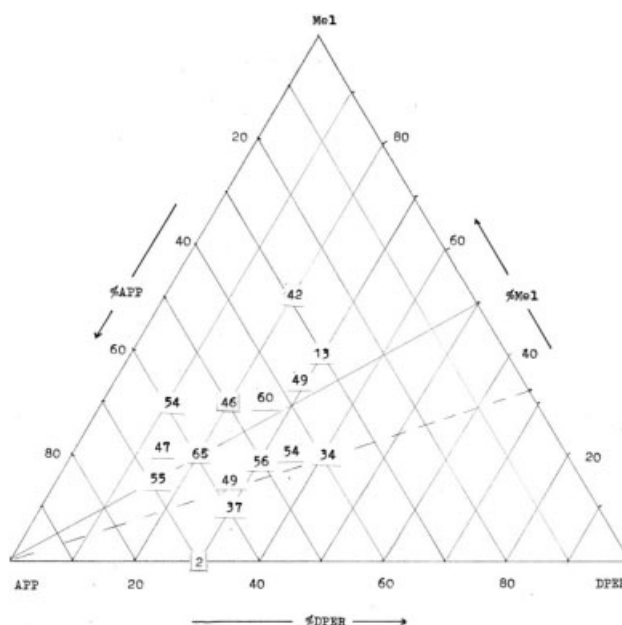


Figure 4 TMA of powder mixtures of APP, DPER, and melamine: figures represent the maximum expansion factor EF max.

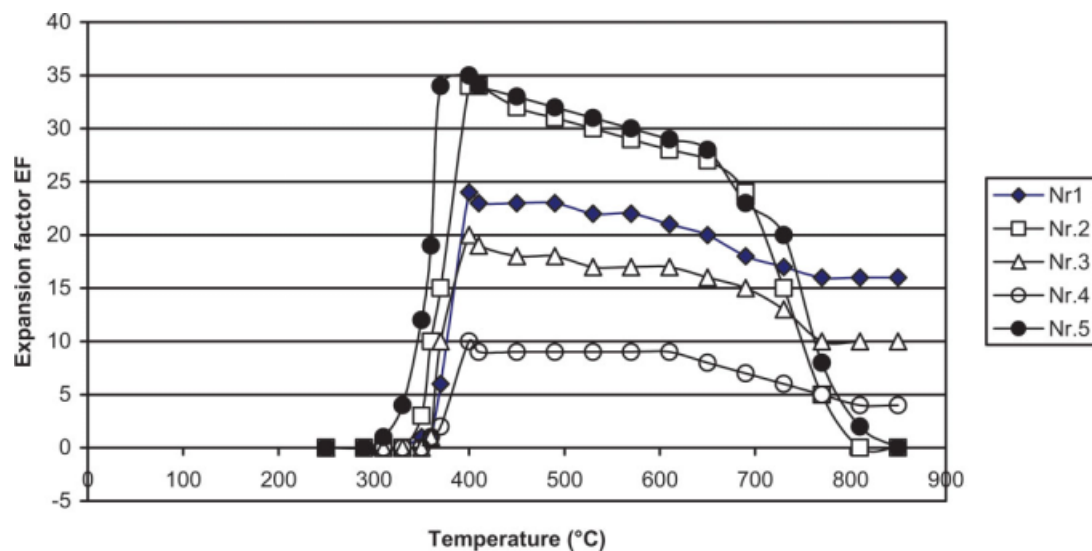


Figure 5 TMA of intumescent paints 1–5 in air at 50 K/min heating rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The weight residue of the dry films of the five paints were investigated in air at a heating rate of 20°C/min in Figure 6. The temperatures of decomposition in Table V were obtained by differentiation of the TGA curves.

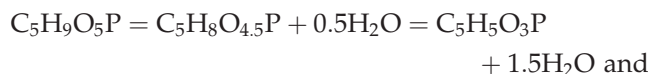
In Figure 7, the dry films of the five paints were subdued to DSC measurements. The observed heats of decomposition h were collected as well as the temperatures of decomposition T and the weight residues in Table V. Because the temperatures of degradation were not independent of the heating rate they were extrapolated to heating rate 0.

At 180°C, the heat of crystal conversion of PER and at 220°C the heat of fusion of DPER was observed. At 250°C, in the presence of PER, DPER or GLY APP decomposed and reacted under evolution of ammonia and heat uptake to phosphoric acid esters. The varnish with the PVC-binder No. 3 degraded under heat evolution. This was explained by the exotherm reaction of ammonia with hydrogen chloride split off from PVC. The relevant esters of polyphosphorus acid with the carbon hydrates and the salts with melamine were expected as reaction products. The measured data were collected in Table VI

The coincidence of temperatures of decomposition at 250°C, 300, 340, 400 and 600 was observed and allowed conclusions on the mechanism of decomposition:

At 300°C, the glycerol phosphoric acid ester GLYP decomposed under heat evolution.

At 340°C, the phosphoric acid esters BCPP ($C_5H_9O_5P$) and DPERP₂ ($C_{10}H_{16}O_9P_2$) degraded under heat evolution. The phosphoric esters were identified as blowing agents because the temperatures of decomposition and of maximum volume increase coincided at 390°C and the theoretical numbers of moles of gasses evolved 2 (PER) and 3 (DPER) corresponded with the measured numbers of 1.7 (PER) and 2.2 (DPER) in powder mixtures



Also surplus APP decomposed to polyphosphoric acid which reacted with melamine further to melamine polyphosphates. At 400°C, melamine

TABLE III
TMA: Expansion of Dry Films Under Air at 50 K/min Heating Rate, Onset Temperature T onset, Maximum Expansion Factor EF Max, and Temperature of Maximum Expansion T_{max} for Intumescent Paints 1–5

Data	No. 1	No. 2	No. 3	No. 4	No. 5
T onset (°C)	350	350	350	350	300
EF max	24	35	20	10	35
T_{max} (°C)	400	400	400	400	400
n mols of gasses	0.8	0.3	0.4	0.3	0.4
w (g)	2838	735	1726	31439	926

TABLE IV
TGA: Temperature of Highest Speed of Decomposition T in Air, From It Derived Energies of Activation EA and Residues R as well as DSC: Heats of Decomposition h in Air at 20 K/min Heating Rate

MW (g/mol)	PER	APP		1mAPP/1mPER			4mAPP/1mPER			
	136	97		233			524			
v (K/min)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)
0	300	325	620	240	340	600	235	330	350	540
5	310	330	630	260	350	630	240	340	390	610
10	330	340	650	280	360	660	250	350	417	675
20	360	360	700	300	370	690	280	360	450	730
40	380	370	770	320	390	750	300	390	480	760
EA (kJ/g)	0.6	1.5	1.1	0.3	0.7	0.5	0.1	0.4	0.2	0.2
R%	0	85	20	73	55	10	88	76	71	15
h (kJ/g)	0.5	0.6	—	0.3	-0.1	—	0.1	0.3	-0.05	—

MW (g/mol)	Mel	1mAPP/1mMel			DPER	1 m APP/1mDPER		
	126	223			254	351		
v (K/min)	T (°C)	T (°C)			T (°C)	T (°C)	T (°C)	T (°C)
20	360	360	600	950	360	240	360	600
R%	0	69	28	5	0	85	39	10
h (kJ/g)	1.0	1.5	—	—	0.5	0.2	-0.2	—

MW (g/mol)	4mAPP/1mDPER			PVAc		PVC		Epoxy
	642			86		62.5		876
v (K/min)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)
20	240	250	360	340	450	270	400	400
EA (kJ/mol/kJ/g)				224/2.6	—	134/2.1	—	67/0.15
R%	84	75	45	35	0	40	10	0
h (kJ/g)	0.15	0.2	-0.3	1.3	0.7	0.6	2.0	2.4

phosphates decomposed and degraded residues of binders as polC_2H_2 decomposed further. At 600°C, the dehydration product of polyphosphoric acid namely phosphoric pentoxide added with titanium oxide to titanium pyrophosphate. In Table V, the values in brackets were the incineration residues at 1000°C, which correlated with calculated values according to the reaction: $\text{TiO}_2 + \text{P}_2\text{O}_5 = \text{TiP}_2\text{O}_7$

Titanium pyrophosphate [13470-09-2] was identified by its UV reflection spectra and by elemental analysis: 21.6% Ti and 27.9% P.

Furthermore, the degradation products of the phosphoric acid esters $\text{C}_5\text{H}_5\text{O}_3\text{P}$ and $\text{C}_{10}\text{H}_{10}\text{O}_6\text{P}_2$ decomposed.

Calorimetry and fire tests

In a calorimeter the heats of combustion were determined for the dry films of the five investigated paints (see Table VII). The binders burned under heat evolution of combustion: PVAc -23 kJ/g, PVC -19 kJ/g and Epoxy -29 kJ/g. As expected, the intu-

mescent paints evolved lower heats of combustion but showed a similar ranking.

The five paints were applied by brush to closed steel columns with a horizontal perimeter to area factor Hp/A of 270 m^{-1} equipped with thermocouples for continuous measurements of temperatures.

The dry film thickness was in every case 1 mm in average. These columns and also one unprotected column were placed in a furnace, which was heated according to the ISO curve. In Figure 6, the temperatures as a function of time are shown.

For the uncoated steel column, the increase of temperature per minute could be calculated by eq. (7)

$$\frac{dT}{\text{min}} = 60 \times a \times (\text{Hp}/\text{A}) \times (\text{T}_{\text{furnace}} - \text{T}_{\text{steel}}) / (c \times \text{Rho}) \quad (7)$$

- a is the heat transfer number for steel 25 ($\text{W}/\text{m}^2\text{K}$)
- c is the heat capacity of steel 460 ($\text{J}/\text{kg}\cdot\text{K}$)
- Rho is the density of steel 7.900 (kg/m^3)

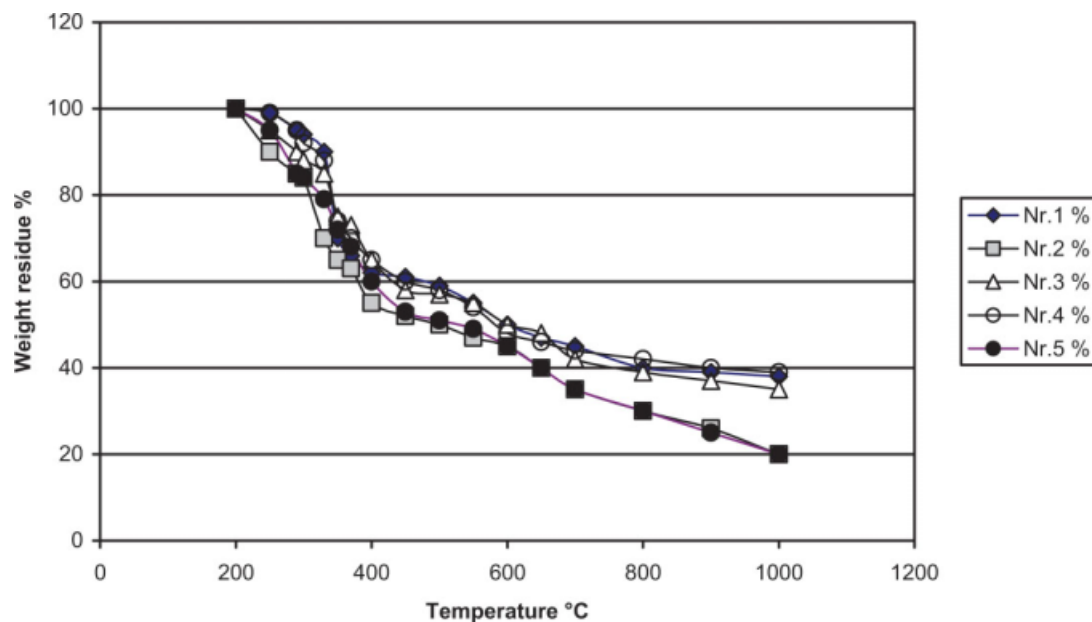


Figure 6 TGA of intumescent paints 1–5 in air at 20 K/min heating rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

When the furnace reached 700°C, the temperature of the unprotected column was 550°C and increased 20°C per minute ($dT/\text{min} = 20 \text{ K/min}$) in Figure 8. According to eq. (7), a raise of temperature of 17°C per minute was calculated

$$\begin{aligned} dT/\text{min} &= 60 \times 25 \times 270 \times (700 - 550) / (460 \times 7.900) \\ &= 17(\text{K/min}) \quad (7a) \end{aligned}$$

For more information the experimental dT/min values were determined using the measured curves by dividing them into three linear segments, which belonged to the unexpanded, to the expanded, and to the expanded charred films (Table VII).

The paint No. 5 protected the column most efficiently. dT/min was a measure of the insulating properties of the films. With the exception of No. 4 all paints exerted similar insulating properties. The poor insulation of No. 4 was caused by its low expansion.

The explanation for the winner No. 5 was given by the shortest onset time of expansion: 3.5 min in comparison with 5 min of the losers.

For the paints No. 1, 2, 3, and 5 the dT/min were the same, namely, 60 K/min for the unexpanded films and 8 K/min for the expanded. The ratio of these inclinations dT_1/dT_2 should correlate with ratio of heat resistances of the expanded and unexpanded films R/R_0 , expressed in eq. (8)

TABLE V
TGA Data in Air and DSC Data in Nitrogen for Intumescent Paints 1–5 at Heating Rates of 0 (extrapolated) and 20 K/min, Temperatures of Decomposition $T^\circ\text{C}$, residues $R\%$ and Heats $h \text{ kJ/g}$

No. 1 $T^\circ\text{C}/R\%/h \text{ kJ/g}$	No. 2 $T^\circ\text{C}/R\%/h \text{ kJ/g}$	No. 3 $T^\circ\text{C}/R\%/h \text{ kJ/g}$	No. 4 $T^\circ\text{C}/R\%/h \text{ kJ/g}$	No. 5 $T^\circ\text{C}/R\%/h \text{ kJ/g}$
0 K/min 221/100/0.05	187/100/0.02	221/100/0.04	221/100/0.03	187/100/0.02
20 K/min 225/100/0.05	190/100/0.02	225/100/0.04	225/100/0.04	190/100/0.02
0 K/min 250/94/0.10	250/84/0.04	250/88/−0.06	250/92/0.10	250/84/0.03
20 K/min 300/94	300/84	300/88	300/92	300/84
0 K/min 340/68/0.20	340/64/0.17	340/74/0.30	340/70/0.20	340/72/0.10
20 K/min 360/68	360/64	360/74	360/70	360/72
0 K/min 400/61/0.01	400/52/−0.12	400/58/0.04	400/60/0.02	400/53/0.05
20 K/min 450/61	450/52	450/58	450/60	450/53
0 K/min 600/45/−	600/35/−	600/42/−	600/44/−	600/45/−
20 K/min 690/45	650/45	650/42	650/44	650/35
(1000/39)	(1000/20)	(1000/35)	(1000/39)	(1000/20)

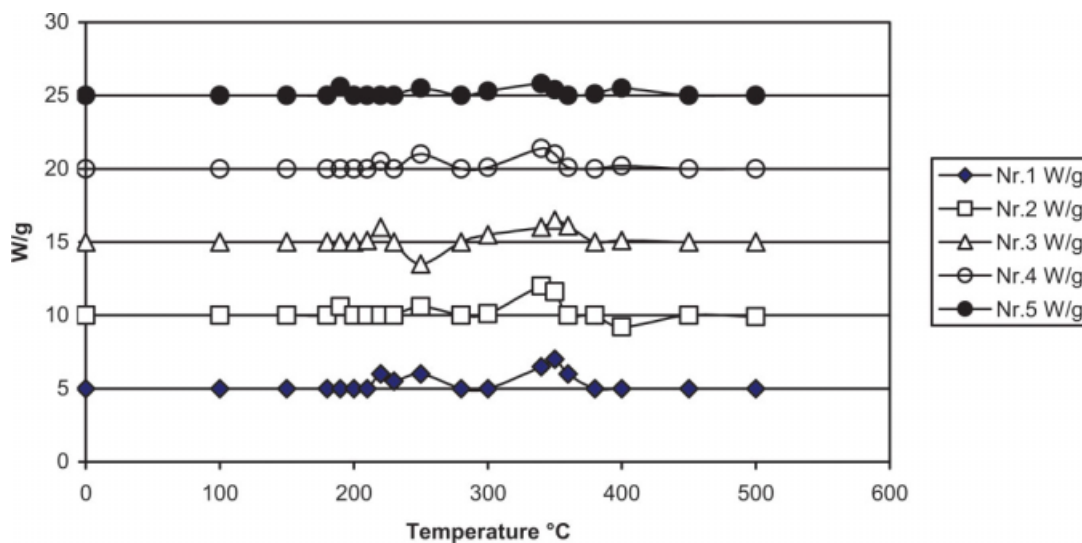


Figure 7 DSC of intumescent paints 1–5 in nitrogen at 20 K/min heating rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$dT1/dT2 = R / R_0 \quad (8)$$

The heat resistance of the unexpanded film is defined by the dry film thickness d_{ft} divided by the heat conductivity λ of the film in eq. (9)

$$R_0 = d_{ft}/\lambda \quad (9)$$

The heat resistance of the expanded film⁹ R is given approximately by eq. (10)

$$R = d_{ft} \cdot (EF \text{ average})^2 / (3 \times \lambda) \quad (10)$$

Introducing the figures of Table VII and complementing eq. (8) by eqs. (9) and (10), eq. (11) was obtained.

$$dT1/dT2 = 60/8 = (EF \text{ average})^2 / 3 \quad (11)$$

As expected, the calculated EF average of 4.7 was smaller than the maximum experimental values EF max of 20–35 in Table III.

DISCUSSION

All binders reduced the expansions of the powder mixtures. The cross-linked epoxies reduced the expansion dramatically and caused extremely poor insulation. The TMA measurements on powders together with the application of ideal gas law lead to 1.7 mols (4 mAPP, 1 mMeI, 1 mPER) and 2.2 mols (4

TABLE VI
Data of Possible Reaction Products of Intumescent Paints

Product	BCPP	DPERP	DPERP2
Formula	C ₅ H ₉ O ₅ P	C ₁₀ H ₁₉ O ₈ P	C ₁₀ H ₁₆ O ₉ P ₂
Molecular weight (g/mol)	180	298	342
Heat of formation (kJ/mol)	–1289	–1915	–2275
Heat of combustion (kJ/g)	–15.1	–18.4	–15.5
T fusion (°C)	215	280	275
T decomposition (°C)	310, 340, 600	340, 600	340, 600
h (kJ/g)	–0.2, –0.2, —	–0.2, —	–0.6, —
R%	90, 80, 27	48, 16	85, 28
Product	Melamine phosphate	Melamine diphosphate	
Molecular weight (g/mol)	224	322	
Heat of formation (kJ/mol)	–1113	–2703	
Heat of combustion (kJ/g)	–8.5	–4.6	
T decomposition (°C)	270, 320, 400, 600, 950	350, 400, 950	
h (kJ/g)	0.16, 0.16, 1.5, —, —	0.5, 2.1, —	
R%	96, 91, 61, 27, 3	90, 52, 5	

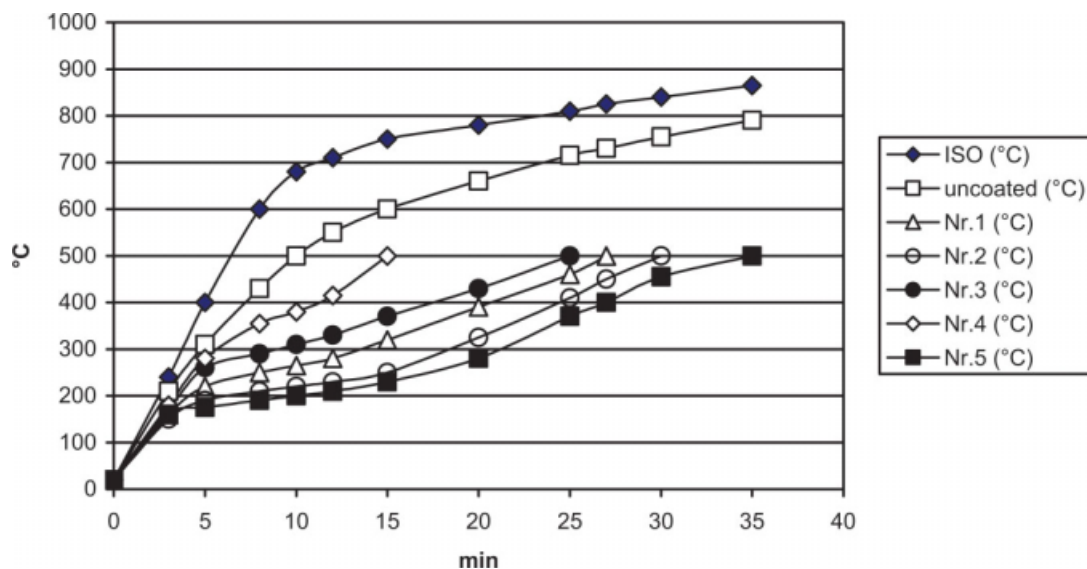


Figure 8 Fire test of intumescent paints 1-5, dft = 1 mm, Hp/A = 270 m⁻¹. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mAPP, 2 mMel, 1 mDPER) of gasses. BCPP split off 2 mols of water and DPERP2 3 mols of water. When gas losses and contra-forces were taken into account, the agreement between theoretically and experimentally determined moles of 2 and 1.7 as well as 3 and 2.2 should be sufficient and indicated these compounds as blowing agents. Furthermore, the temperatures of decomposition and those of maximum volume increase coincided for BCPP with 340°C for DPERP2 with 340°C and for GLYP with 300°C.

The burning test pointed out the importance of the early foaming for the insulation.

The experimental results of TGA and DSC measurements indicated the main steps of degradation. In the following the attempt was made to set up chemical equations as well as balances of heats of formation and balances of masses to describe the reactions during the steps of decomposition at 250, 340, 400, 600, and 900°C. To set up complete balances of heats of formation, the unknown heats of formation had to be determined from published or calorimetrically measured heats of combustion. Not all data from

literature were reliable, for instance, the heat of combustion of DPER cited as -30.4 kJ/g in¹⁰ was much too high.

Balances of heats of formation and masses

The molecular weights (MW), the heats of formation (Hf), the heats of combustion hcomb, the heats of crystal rearrangement as well as heats of melting h and the heats of decomposition hdec of the ingredients are summarized in Table VIII. In Table VIII, n.d. was the abbreviation for not determined. In the balances the formula F, the molecular weights MW, the heats of formation Hf were later taken into account.

In Table I, the stoichiometric formulations of the paints were described by the number of moles of reactants. For instance paint No. 1 comprised 12 moles APP, 1 mol DPER, 2 moles melamine, 5 moles PVAc, and 6 moles TiO₂.

Under the excess of oxygen paint No. 1 burned to the products of highest oxidation under evolution of

TABLE VII
Results of Calorimetric Measurements: Heats of Combustion h Comb and Fire tests:
The Curve of Figure 8 Divided into Three Linear Segments

No.	h comb kJ/g	dT1/min×t		dT2/min×t		dT3/min×t		Sum	
		Unexpanded	Expanded	Expanded	Expanded	Charred expanded film	T (°C)	min	
1	-7.8	60 × 5 = 300	8 × 10 = 80	8 × 10 = 80	8 × 10 = 80	9 × 12 = 108	488	27	
2	-11.5	60 × 4 = 240	8 × 12 = 96	8 × 12 = 96	8 × 12 = 96	11 × 14 = 144	490	30	
3	-9.1	60 × 5 = 300	8 × 8 = 64	8 × 8 = 64	8 × 8 = 64	10 × 12 = 120	484	25	
4	-13.7	60 × 5 = 300	18 × 3 = 54	18 × 3 = 54	18 × 3 = 54	20 × 7 = 140	494	15	
5	-10.6	60 × 3.5 = 210	8 × 14.5 = 116	8 × 14.5 = 116	8 × 14.5 = 116	11 × 15 = 165	491	33	

TABLE VIII
Data of Ingredients of Intumescent Paints 1–5

Product	PER	DPER	APP	Mel	TiO ₂	PVAc	PVC	Epoxy
Formula	C ₅ H ₁₂ O ₄	C ₁₀ H ₂₂ O ₇	NH ₄ PO ₃	C ₃ H ₆ N ₆	TiO ₂	C ₄ H ₆ O ₂	C ₂ H ₃ Cl	C ₅₅ H ₆₈ N ₂ O ₇
MW (g/mol)	136	254	97	126	80	86	62.5	876
Hf (kJ/mol)	-913	-1313	-1085	-72	-915	-450	-20	-6400
hcomb (kJ/g)	-20.3	-21.4	-2.1	-15.6		-23	-19	-29
T (°C)	187cryst.261 fus	221 fus.		360 sub.		30 glass	130 fus.	
h (kJ/g)	0.32, 0.04	0.38		1			0.05	
Tdec (°C)	360	360	330, 600	360		340, 450	270, 400	400
hdec (kJ/g)	0.5	0.5	0.6, 1.0	1		1.3, 0.7	0.6, 2.0	2.4
EA (kJ/g)	0.6		1.5, 1.0			2.6, n.d.*	2.1, n.d.	0.15

the heat of combustion *h*. The formula *F*, the balance of masses *MW* and of heats of formation *H* were given in eq. (12) for combustion

$$\text{Combustion : hexp/cal} = -7.8 / -7.8 \text{ kJ/g;} \\ \text{Rexp/cal} = 45/47\% \quad (12)$$

- F1: 12 APP + C₁₀H₂₂O₇ + 2Mel + 5C₄H₆O₂ + 6TiO₂ + 76.5O₂=
- MW1 (g/mol): 12 × 97 + 1 × 254 + 2 × 126 + 5 × 86 + 6 × 80 + 76.5 × 32 = 5028
- H1 (kJ/mol): 12 × -1085 + -1313 + 2 × -72 + 5 × -450 + 6 × -915 = -22.217
- F2: 6TiP₂O₇ + 24NO₂ + 36CO₂ + 56H₂O
- MW2 (g/mol): 1332 + 1104 + 1384 + 1008 = 5028
- H2 (kJ/mol): 6 × -2500 + 24 × 34 + 36 × -393 + 56 × -286 = -44.348

$$\text{-----} \\ \text{H2} - \text{H1} = -22.131$$

The balance of weight (MW1 = MW2) was fulfilled. The difference of the heats of formation was the molar heat of combustion of -22.131 kJ/mol or divided by the molecular weight 5028 g/mol -7.8 kJ/g. The calculated residue amounted $(6 \times 220 / 2828) \times 100 = 47\%$.

As intumescence impeded the contact with air the reactions of degradation were the same as those of pyrolysis under nitrogen. The formula *F* and the balances of masses and heats of formation were established for the separate steps of decomposition at 250, 340, 400, 600, and 900°C:

At 250°C, 2 moles of APP reacted with 1 mole of DPER to the phosphoric acid ester C₁₀H₁₆O₉P₂

$$250^\circ\text{C hexp/cal} = 0.1/0.09 \text{ kJ/g;} \text{ Rexp/cal} = 94/93\% \\ (13)$$

- F3: 2APP + C₁₀H₂₂O₇ = C₁₀H₁₆O₉P₂ + 2NH₃ + 4H₂O
- MW3: 2 × 97 + 254 = 342 + 2 × 17 + 4 × 18
- H3: 2 × -1085 + -1313 + 250 = -2169 + 2 × -46 + 4 × -243

The weight balance determined the weight loss $(2 \times 17 + 4 \times 18) \times 100 / 2838\%$ or the weight residue $(100 - \text{weight loss})$. In this case, calculated 93% compared with 94% found. The heats of formation were in balance when a heat of decomposition of 250 kJ/mole or $250 / 2828 = 0.09$ kJ/g was considered, which compared with 0.1 kJ/g experimental heat of decomposition.

At 340°C, the synthesized phosphoric acid ester decomposed under heat evolution and foaming. APP in excess decomposed to polyphosphoric acid, which reacted further to the melamine salt Mel(HPO₃)₂. PVAc split off acetic acid and polyacetylene¹¹ polC₂H₂ remained. These events were summarized in eq. (14)

$$340^\circ\text{C hexp/cal} = 0.20/0.30; \text{Rexp/cal} \\ = 68 / (73.9 - 0.5 \times 9.1 \text{ additives}) = 69.35\% \quad (14)$$

- F4: C₁₀H₁₆O₉P₂ + 5C₄H₆O₂ + 10APP + 2Mel =
- MW4: 342 + 5 × 86 + 10 × 97 + 2 × 126 = 1994
- H4: -2169 + 5 × -450 + 10 × -1085 + 2 × -72 + 841 = -14.572
- F5: C₁₀H₁₀O₆P₂ + 3H₂O + 5CH₃COOH + 5 polC₂H₂ + 10NH₃ + 6HPO₃ + 2Mel(HPO₃)₂
- MW5: 288 + 3 × 18 + 5 × 60 + 5 × 26 + 10 × 17 + 6 × 80 + 2 × 286 = 1994
- H5: -1614 + 3 × -242 + 5 × -439 + 5 × 147 + 10 × -46 + 6 × -981 + 2 × -2214 = -14.572

With the already explained procedure, the calculated residue and the heat changes were determined. To obtain a better fit of residue, *R*, the loss of half of the used additives was assumed.

At 400°C, the melamine dipolyphosphate decomposed under evolution of nitrogen and water and the residue 3C+NPO.^{9,11} In the same range of temperature, the polyacetylene chain was cracked to methane and carbon¹¹ [see eq. (15)].

$$400^\circ\text{C hexp/cal} = 0.01/0.01; \\ \text{R} = 61 / (57.85 - 0.5 \times 9.1 \text{ additives}) = 53.3\% \quad (15)$$

TABLE IX
Comparison of Experimental and Calculated Residues R and Heats h for Intumescent Paints 1–5

T (°C) R h	No. 1 Exp	No. 1 Calc	No. 2 Exp	No. 2 Calc	No. 3 Exp	No. 3 Calc	No. 4 Exp	No. 4 Calc	No. 5 Exp	No. 5 Calc
250 R%	94	93	84	85	88	90	92	92	84	89
250 h kJ/g	0.1	0.09	0.04	0.03	-0.06	-0.07	0.1	0.13	0.03	0.04
340 R%	68	69	64	63	74	78	70	73	72	68
340 h kJ/g	0.2	0.3	0.17	0.17	0.3	0.25	0.2	0.2	0.15	0.12
400 R%	61	53	52	52	58	59	60	60	53	50
400 h kJ/g	0.01	0.01	-0.12	-0.17	0.04	0.04	0.02	0.01	0.05	0.07
600 R%	45	41	35	36	42	39	44	45	35	35
900 R%	39	38	20	20	35	34	35	35	20	20

- F6: $2\text{Mel}(\text{HPO}_3)_2 + 5 \text{ polC}_2\text{H}_2 = 4\text{NPO} + 8\text{H}_2\text{O} + 2.5\text{CH}_4 + 13.5\text{C} + 4\text{N}_2$
- MW6: $2 \times 286 + 5 \times 26 = 4 \times 61 + 8 \times 18 + 2.5 \times 16 + 13.5 \times 12 + 4 \times 28$
- H6: $2 \times -2047 + 5 \times 147 + 27.5 = 4 \times -302 + 8 \times -242 + 2.5 \times -75$

For a better fit, the assumption was made that the last half of additives was evaporated.

At 600°C, the degraded phosphoric acid ester $\text{C}_{10}\text{H}_{10}\text{O}_6\text{P}_2$ decomposed to 2 moles of methane and polyphosphoric acid, which reacted with titanium oxide to titanium pyrophosphate.

$$600^\circ\text{C h}_{\text{exp}}/\text{calc} = -/0.07 \text{ kJ/g}; \quad \text{R}_{\text{exp}}/\text{calc} = 45/41\% \quad (16)$$

- F7: $\text{C}_{10}\text{H}_{10}\text{O}_6\text{P}_2 + 6\text{HPO}_3 + 4\text{TiO}_2 = 4\text{TiP}_2\text{O}_7 + 2\text{CH}_4 + 4\text{H}_2\text{O} + 8\text{C}$
- MW7: $288 + 6 \times 80 + 4 \times 80 = 4 \times 222 + 2 \times 16 + 4 \times 18 + 8 \times 12$
- H7: $-1614 + 6 \times -981 + 4 \times -915 + 42 = 4 \times -2500 + 2 \times -75 + 4 \times -242$

At 900°C, the last instable product $\text{NPO}^{12,13}$ decomposed to the gasses oxygen and phosphorus nitride¹⁴ in eq. (17)

$$900^\circ\text{C h}_{\text{exp}}/\text{cal} = -/0.31; \quad \text{R}_{\text{exp}}/\text{calc} = 39/38\% \quad (17)$$

- F8: $4(\text{NPO} = \text{PN} + 0.5\text{O}_2)$
- MW8: $61 = 45 + 16$
- H8: $-302 + 217 = -85$

The overall reaction was the sum of the single steps of degradation at 250, 340, 400, 600 and 900°C and was summarized in eq. (18)

$$\text{Over all decomposition h}_{\text{exp}}/\text{calc} = 0.7/0.83 \text{ kJ/g}; \quad \text{R}_{\text{exp}}/\text{calc} = 39/38\% \quad (18)$$

- F9: $12 \text{ APP} + \text{C}_{10}\text{H}_{22}\text{O}_7 + 2\text{Mel} + 5\text{C}_4\text{H}_6\text{O}_2 + 6\text{TiO}_2 =$

- MW9: 2580
 - H1: -22.217
 - F10: $12\text{NH}_3 + 19\text{H}_2\text{O} + 5\text{CH}_3\text{COOH} + 4.5\text{CH}_4 + 4\text{TiP}_2\text{O}_5 + 2\text{TiO}_2 + 4\text{PN} + 21.5\text{C} + 4\text{N}_2 + 2\text{O}_2$
 - MW10: $204 + 342 + 300 + 72 + 888 + 160 + 180 + 258 + 112 + 64 = 2580$
 - H10: $12 \times -46 + 19 \times -242 + 5 \times -439 + 4.5 \times -75 + 4 \times -2500 + 2 \times -915 + 4 \times -85 = -19.852.5$
-
- $$(\text{H1}-\text{H10}) = -2.364.5$$

The fit of the calculated heats of decomposition and weight losses with those determined by experiments was a measure for the quality of the chemical description in Table IX.

CONCLUSION

Stoichiometrically formulated paints were described by chemical formula together with balances of heats of formations—determined from heats of combustion—and balances of masses. Calculated heats of reactions and weight residues fitted well with those measured by TGA and DSC. The coincidence of temperatures of decomposition with those of maximum volume increase as well as the correspondence of measured and theoretically determined moles of gasses evolved identified the cyclic phosphoric acid esters of pentaerythritol dipentaerythrol and glycerol as the blowing agents for intumescent paints. The new stoichiometric approach allowed a better insight and led to a promising improvement: added glycerol reacted with polyphosphoric acid to a phosphoric acid ester with a low temperature of decomposition and to a paint with the best performance in the fire test. Melamine reacted with polyphosphoric acid to the salts. Phosphorus pentoxide formed by dehydration of polyphosphoric acid reacted with titanium dioxide to titanium pyrophosphate.

From the current point of view, further improvements should be possible by increasing the gas yield and by replacing phosphoric esters with high temperatures of degradation by those of lower temperatures of decomposition.

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